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(54) **Polyphenylene ether based moulding composition.**

(57) Moulding composition having an extremely good combination of physical-mechanical, tensile and thermal properties, comprising a polyphenylene ether and a high-impact vinyl-aromatic polymer constituted by a blend of a polymodal vinyl aromatic monomer-conjugated diene block polymer and a high-impact vinyl-aromatic polymer containing, dispersed in it, a dienic rubber, in the form of particles having a cellular structure and an average chord of at least 1.2 micrometres.

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The present invention relates to a polyphenylene ether-based moulding composition.

More particularly, the present invention relates to a polyphenylene ether-based moulding composition displaying a good balance of physical-mechanical properties, such as (IZOD) resilience, as well as tensile and thermal characteristics, e.g., VICAT softening point.

Polyphenylene ether resins (PPE), also known as "polyphenylene oxide resins" are a well-known class of engineering polymers and are disclosed in a number of patents, such as, e.g., in U.S. patent Nos. 3,306,874, 3,306,875, 3, 257,357 and 3,257,358, all incorporated thereto by reference. They are useful for many applications, in which a high heat resistance is required and, by being thermoplastic, they can be fabricated into formed articles by means of injection or extrusion moulding techniques.

Notwithstanding this very large number of potential commercial applications of polyphenylene ether resins, their use is limited owing to their poor processability, mainly due to their relatively high viscosity in the molten state; and to their narrow processability range, which may cause difficulties during the extrusion and injection moulding operations.

Furthermore, the high temperatures required in order to soften the polymer and the problems associated with such high temperatures, such as instability and discolouration, render the techniques of extrusion and injection moulding not very much actractive from an industrial viewpoint.

A further drawback is that the polyphenylene ether resins display a poor solvent resistance after being formed and a low (IZOD) resilience, so their use for certain applications is still more limited.

In order to overcome these drawbacks, blending polyphenylene ether resins with other polymers displaying the properties such resins lack, was proposed.

So, e.g., U.S. patent No. 3,379,792 proposes to improve the fluidity of polyphenylene ether resins by means of the addition of a polyamide. However, according to the teaching of this patent, the blends are limited to a polyamide concentration of not more than 25% by weight; in fact, a further amount of polyamide causes delamination and an appreciable decay of the other physical-mechanical properties, such as resilience.

According to U.S. patent No. 3,361,851, the impact strength and the resistance to chemical agents of polyphenylene ether can be improved by adding a polyolefin.

U.S. patent No. 3,383,435 teaches that polyphenylene ether is compatible, in all proportions, with polystyrene resins, also including those modified with rubber in order to give them impact strength properties, and that the resulting compositions display improvements in many properties, as compared to those of each component and an improved processability. Preferred embodiments of U.S. patent No. 3,383,435 are those compositions which comprise a high-impact polystyrene (HIPS) and a poly(2,6-dialkyl-1,4-phenylene) ether. These compositions are important from the commercial viewpoint, because they make it possible improvements to be obtained both in processability of polyphenylene ether in the molten state, and in the impact strength of the formed articles which can be obtained from such compositions. Furthermore, by adjusting the ratio of both polymers to each other, compositions can be obtained which display predetermined properties, falling between those of polystyrene resins and those of polyphenylene ether.

A drawback displayed by these compositions is that the use of grafted rubber-modified high impact polystyrene, such as, e.g., LUSTREX HT-88, used in Example 7 of U.S. patent No. 3,383,435, implies an improvement in toughness, but to the damage of clearness.

In order to remove this drawback, U.S. patent Nos. 4,373,064 and 4,513,120 propose to mix polyphenylene ether with a particular type of high-impact polystyrene. Such a polystyrene comprises a polystyrenic matrix in which a discontinuous phase comprising particles of a styrene homopolymer embedded in a membrane of a dienic rubber, is uniformly dispersed; herein such particles have an average size comprised within the range of from 0.1 to 0.7 micrometres and the thickness of the membrane is not higher than half-diameter of the relevant particle. The rubber content is comprised within the range of from 1 to 10% by weight, based on rubber-modified polystyrene. The resulting compositions contain at least two phases, one of which is discontinuous and comprises the polystyrene particles embedded inside the rubber, and the other phase is continuous and comprises the polyphenylene ether and the polystyrene.

Unfortunately, also these compositions are not free from drawbacks. In fact, the improvement in toughness and clearness are obtained to the damage of heat resistance or VICAT softening point, what limits the use of these compositions in particular application sectors in which such a feature is required.

The present Applicant has surprisingly found now that a particular type of high-impact polystyrene resins, constituted by a blend of a polymodal vinyl aromatic monomer-conjugated diene block polymer and a high-impact vinyl aromatic polymer containing, dispered in it, a dienic rubber in the form of particles having a cellular structure and an average chord of at least 1.2 micrometres, is compatible, in all proportions, with polyphenylene ether, to yield compositions displaying a very good combination of

physical-mechanical properties, such as (IZOD) resilience, as well as tensile and thermal properties, such as VICAT softening point.

In its widest aspect, the present invention relates to a moulding composition having a very good combination of physical-mechanical, tensile and thermal properties, comprising:

(C_1) a polyphenylene ether, and

(C_2) a high-impact vinyl aromatic polymer constituted by a blend of

(i) a polymodal vinyl aromatic monomer-conjugated diene block polymer, having a content of vinyl aromatic monomer comprised within the range of from 55 to 85% by weight, and

(ii) a vinyl-aromatic polymer containing from 5 to 15% by weight, based on said polymer, of a dispersed dienic rubber in the form of particles having a cellular structure and an average chord of at least 1.2 micrometres.

The proportions of both components (C_1) and (C_2) in the moulding composition according to the present invention may vary within a wide range, even if said component (C_1) is generally present in amounts of at least 1% by weight, and said component (C_2) is present in amounts of at least 20% by weight, based on total composition.

Compositions which have proved to be particularly advantageous for the purposes of the present invention are those containing:

* from 5 to 60% by weight of polyphenylene ether (C_1) and, correspondingly
* from 95 to 40% by weight of the high-impact vinyl aromatic polymer (C_2).

Preferably, the best results as regards IZOD resilience and VICAT softening point have been obtained when the compositions according to the present invention contained:

* from 20 to 45% by weight of polyphenylene ether (C_1) and, correspondingly
* from 80 to 55% by weight of high-impact vinyl aromatic polymer (C_2);

with said percent levels being referred to the total weight of the blend.

In the high-impact vinyl aromatic polymer (C_2), the weight ratio of components (i) and (ii) to each other is not critical for the purposes of the present invention. In general, the high-impact vinyl aromatic polymer (C_2) contains from 30 to 90% by weight of polymodal block polymer (i) and, correspondingly, from 70 to 10% by weight of vinyl aromatic polymer (ii) containing the dienic rubber in the form of dispersed particles.

A particularly preferred high-impact vinyl aromatic polymer (C_2) in the compositions according to the present invention is the one which contains from 50 to 85% by weight of the polymodal block polymer (i) and, correspondingly, from 50 to 15% by weight of the high-impact vinyl aromatic polymer (ii).

The expression "polymodal block copolymer" (i), as used in the present disclosure and in the appended claims, comprises the polymeric products which contain at least two blocks with different molecular weights prevailingly constituted by a vinyl aromatic monomer, and at least one block prevailingly constituted by a conjugated diene.

These polymodal block polymers can either be of linear type, or of radial type.

The polymodal linear block polymers can be represented by one of the following general formulae (I) or (II):

(I) S_1-B-S_2;

(II) B_1-S_1-B_2-S_2;

in which: S_1 and S_2 are non-elastomeric polymeric blocks of a vinyl aromatic monomer having different molecular weights; and B, B_1 and B_2 are elastomeric polymeric blocks based on a conjugated diene, having the same, or different molecular weights. These polymodal linear block polymers are already known from relevant technical literature and are disclosed, e.g., in U.S. patent No. 3,265,765.

In these polymodal linear block polymers, the non-elastomeric polymeric blocks have a molecular weight comprised within the range of from 5,000 to 250,000, and the elastomeric blocks have a molecular weight comprised within the range of from 2,000 to 250,000. Between the polymeric blocks S_1, S_2 and B, B_1 and B_2, "random" and/or "tapered" portions can be present.

In the "tapered" portion, the transition between B, B_1 and B_2 blocks, and S_1 and S_2 blocks can be gradual, in the sense that the proportion of the vinyl aromatic monomer in the dienic polymer progressively increases in the direction of the non-elastomeric polymeric block, while, accordingly, the proportion of conjugated diene progressively decreases. In the "random" portion, the vinyl aromatic and conjugated diene monomers follow each other haphazardly. The molecular weights of the "random" and/or "tapered" portions are preferably comprised within the range of from 500 to 50,000.

These polymodal linear block polymers can be prepared according to well-known techniques for those skilled in the art, such as, e.g., firstly forming a block of vinyl aromatic polymer, by anionic polymerization, in an inert solvent and in the presence of a lithium-based metal-organic catalyst (initiator), then forming the conjugated diene polymer block by adding such a conjugated diene monomer to the polymerization mixture and subsequently forming another block of vinyl aromatic polymer by means of the addition of vinyl aromatic monomer.

The preparation of the polymodal linear block polymers is carried out in an inert hydrocarbon solvent, such as penthane, hexane, benzene, cyclohexane, and so forth, at a temperature comprised within the range of from 40 °C to 120 °C in the presence of catalytic amounts of an alkyl-, cycloalkyl- or aryl-lithium compound, such as, e.g., methyl-lithium, n-butyl-lithium, sec.-butyl-lithium, cyclohexyl-lithium, phenyl-lithium, and so forth.

The polymodal linear block polymers are available from the market, such as, e.g., those products manufactured and marketed under "FINACLEAR(R) 520" trade mark, by the company Fina.

The radial polymodal block polymer is also of known type available from the market. Such a polymodal radial block copolymer can be of the following types:

(III) $(S_1\text{-}S_2\text{-}B_1)_n - X - (B_1 - S_2)_m$;

(IV) $(S_1\text{-}S_2/B_1\text{-}B_2)_m - X - (B_2\text{-}B_1/S_2)_n$;

(V) $(S_1\text{-}S_2\text{-}B_1/S_3\text{-}B_2)_m - X - (B_2\text{-}S_3/B_1\text{-}S_2)_n$;

(VI) $(S_1\text{-}B_1 \rightarrow S_2)_n - X - (S_2 \leftarrow B_1)_m$;

(VII) $(S_3\text{-}S_4\text{-}B_2 \rightarrow S_5)_n - X - (S_5 \leftarrow B_2\text{-}S_4)_m$

(VIII)
$$\begin{array}{l} (S_6\text{-}S_7\text{-}B_3\text{-}S_8\text{-}B_4)_p \\ \qquad\qquad\qquad\qquad\qquad\quad \backslash \\ (S_7\text{-}B_3\text{-}S_8\text{-}B_4)_q\text{-}X \\ \qquad\qquad\qquad\qquad\qquad\quad / \\ \qquad\qquad\qquad\qquad (S_8\text{-}B_4)_r \end{array}$$

wherein:

S_1, S_2, S_3, S_4, S_5, S_6, S_7 and S_8	are non-elastomeric polymeric blocks, of a vinyl-aromatic monomer, each having different molecular weights, thus yielding bimodal, trimodal, or, in general, polymodal blocks;
B_1, B_2, B_3 and B_4	are elastomeric polymeric blocks based on a conjugated diene, having the same molecular weight or different molecular weights from one another;
X	is the radical of a polyfunctional coupling agent, by means of which the block copolymers forming the arms are chemically coupled with one another;
m and n	are integers, with m being larger than n, and the sum of which is larger than 3, generally comprised within the range of from 3 to 10 and preferably is either 3 or 4, and corresponds to the functionality of radical X; and
p, q and r	are integers the sum of which is larger than 3, generally comprised within the range of from 3 to 10 and preferably is either 3 or 4, and corresponds to the functionality of radical X; and
S_2/B_1, B_1/S_2, B_1/S_3 and S_3/B_1	are blocks of copolymers, of either "random" and/or "tapered" type, of vinyl aromatic monomer and conjugated diene.

The symbol "→" of formulae (VI) and (VII) means that the transition between the polymeric blocks takes place gradually ("tapered"), rather than sharply, in the sense that the proportion of the vinyl aromatic

monomer in the dienic polymer progressively increases in the direction of the non-elastomeric polymeric block, while the proportion of conjugated diene progressively decreases accordingly.

The coupling agent "X" is well-known from technical literature and is disclosed, e.g., in British patent No. 985,614. Typical examples for coupling agents are polyepoxides, such as, e.g., epoxidated polybutadiene; epoxidated linseed oil; polyesters, such as diethyl adipate; polyhalides, such as silicon tetrachloride; polyisocyanates, such as benzene 1,2,4-triisocyanate; polyimines; polyaldehydes; polyketones, such as 1,3,6-hexanetrione; polyanhydrides, such as pyromellitic dianhydride; polycarboxy acid halides, such as mellitoyl chloride; polyvinyl aromatic compounds, as disclosed in U.S. patent No. 3,280,824.

The preparation of these polymodal radial block polymers is carried out by means of well known techniques, by firstly forming the linear block copolymer containing active lithium atoms at a chain end, as disclosed above for polymodal linear block polymers, and subsequently adding the coupling agent having at least three functional groups capable of reacting with lithium-carbon bonds, so as to link the carbon atoms chain to the functional group.

In these polymodal radial block polymers, the non-elastomeric polymeric blocks have a molecular weight comprised within the range of from 5,000 to 250,000, the elastomeric blocks have a molecular weight comprised within the range of from 5,000 to 50,000, the blocks of copolymers of "random" and/or "tapered" types have a molecular weight comprised within the range of from 500 to 50,000, and the $B_1 \rightarrow S_2$ and $B_2 \rightarrow S_5$ blocks preferably have a molecular weight comprised within the range of from 10,000 to 100,000.

These polymodal radial block polymers are well-known in technical literature; so, e.g., the polymers of formula (III) are disclosed in U.S. patent No. 4,403,074; the polymers of formula (IV) are disclosed in U.S. patent No. 4,221,884; the polymers of formula (V) are disclosed in published European patent application with publ. No. 0,255,001; U.S. patent Nos. 4,086,298 and 4,167,545 disclose the polymers of formula (VI) and (VII) and EPO patent No. 0,153,727, the polymers of formula (VIII).

The polymodal radial block polymers are available from the market from several manufacturers such as, e.g., from BASF under STYROLUX(R) trade mark, or from Phillips Petroleum under K-RESIN(R) trade mark.

The useful conjugated dienes for preparing the polymodal either linear or radial block polymers (i) are those containing from 4 to 8 carbon atoms in their molecule, such as, e.g., 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene,pyperilene and mixtures thereof.

1,3-butadiene is particularly preferred.

The high-impact vinyl aromatic polymer (ii) can be prepared by means of any conventional techniques to produce crosslinked high-impact polymers, such as, e.g., by bulk polymerization, solution, suspension, emulsion and bulk-suspension polymerization. These polymers are produced from a vinyl aromatic monomer and a dienic rubber. The conventional technique consists in dissolving the dienic rubber in the vinyl aromatic monomer and then submitting the mixture to polymerization, in the presence of a catalyst, to produce a vinyl aromatic polymer containing the dienic rubber copolymerized by grafting.

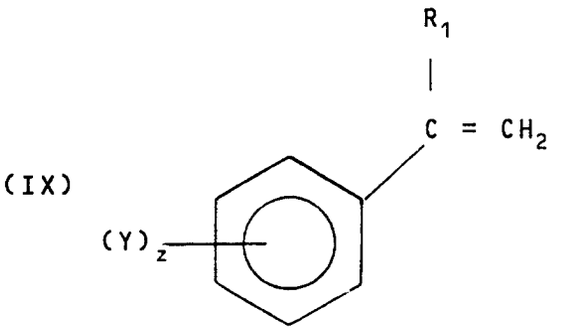
The size of the particles of the rubbery phase is regulated by means of the amount of the grafted phase, the revolution speed (rpm) of the stirrer of the reactor inside which the phase reversal takes place and/or by adjusting the amount of the chain transfer agent, as those skilled in the art are well aware of (see: G.F. Freeguard, British Pol. J. 1974, 6, pages 205-228; and A. Echte, Rubber Toughened Plastics 1989, pages 15-63, Publisher American Chemical Society.

The average chord of the particles is the d_{50} of the cumulated mass distribution. It is determined according to methodologies well known to those skilled in the art, by measuring the particles under the transmission electronic microscope, as described in F. Lenz Mikroskopie 63 (1956) 50-56.

The average chord of the particles of the dienic rubber can be comprised within the range of from 1.2 to 15, preferably of from 1.5 to 10 micrometres.

The dienic rubber incorporated in the vinyl aromatic polymer (II) in order to endow it with high-impact characteristics, may be of either natural or synthetic origin. Suitable synthetic dienic rubbers are those constituted by a polymer of a conjugated diene having from 4 to 6 carbon atoms, and, in particular, polybutadiene, high-cis and medium-cis polybutadiene and low viscosity polybutadiene, polyisoprene, butadiene and/or isoprene copolymers with styrene or other monomers containing more than 50% by weight of butadiene or isoprene. The amount of dienic rubber incorporated to the polymer may range from 5 to 15%, preferably from 7 to 12% by weight.

The expression "vinyl aromatic monomer", as used in the present disclosure and in the appended claims, relates in general to all of the monomers having the general formula (IX):



wherein:

R_1 represents a hydrogen atom or a C_1-C_4 alkyl radical;

Y represents a hydrogen atom, a halogen atom, or a C_1-C_4 alkyl radical, and

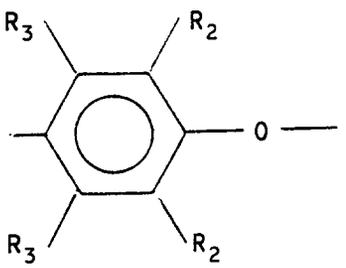
z is zero or an integer comprised within the range of from 1 to 5.

Examples of vinyl aromatic monomers having the above reported general formula (IX) are: styrene, methylstyrene, mono-, di-, tri-, and penta-chlorostyrene and the corresponding α-methylstyrenes, alkylated-ring styrenes and corresponding α-methylstyrenes, such as ortho- and para-methylstyrenes, ortho- and para-ethylstyrenes, ortho- and para-methyl-α-methylstyrenes, and so forth. These monomers can be used either alone or as mixtures with each other or with other copolymerizable comonomers, such as, e.g., maleic anhydride, acrylonitrile, methacrylonitrile, alkyl esters of acrylic or methacrylic acid.

Styrene is particularly preferred.

The polyphenylene ether (C_1), used in the compositions according to the present invention, is a well-known polymer or copolymer, widely used in industry, in particular as an engineering polymer, in those applications in which toughness and heat resistance are required.

The polyphenylene ethers are polymers and copolymers comprising a plurality of structural units of formula (X) :



(X)

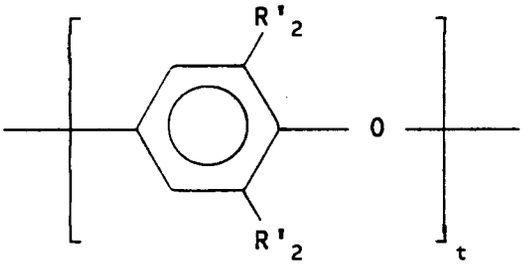
wherein:

each R_2 independently is a halogen atom, a primary or secondary C_1-C_7 alkyl, substituted alkyl, phenyl, substituted phenyl, C_1-C_7 alkyloxy or halo-alkyloxy radical in which at least two carbon atoms separate the halogen and oxygen atoms; and

each R_3 independently is a hydrogen atom, a halogen atom, a primary or secondary C_1-C_7 alkyl, substituted alkyl, phenyl, substituted phenyl, C_1-C_7 alkyloxy or halo-alkyloxy radical, as defined for R_2.

Examples for R_2 and R_3 comprise: hydrogen; a halogen, such a chlorine, bromine or fluorine; an alkyl or substituted alkyl radical, such as methyl, ethyl, n.- and iso-propyl, n., sec., iso- and tert.-butyl, n.amyl, n.hexyl, 2,3-dimethylbutyl, chloroethyl, hydroxyethyl, phenylethyl, hydroxymethyl, carboxyethyl, methoxycarbonylethyl, cyanoethyl; aryl or substituted aryl radicals, such as phenyl, chlorophenyl, methylphenyl, dimethylphenyl, ethylphenyl; a benzyl radical or an allyl radical.

Preferred polyphenylene ethers in the present invention are those having the general formula (XI):



(XI)

wherein the radicals

R'_2 independently are an alkyl radical having from 1 to 4 carbon atoms and

t is at least 50 and preferably is comprised within the range of from 60 to about 600.

Illustrative examples of particularly suitable polyphenylene ethers for the present invention are:

-- poly (2,6-dimethyl-1,4-phenylene)ether;
-- poly (2,6-diethyl-1,4-phenylene)ether;
-- poly (2-methyl-6-ethyl-1,4-phenylene)ether;
-- poly (2,6-dipropyl-1,4-phenylene)ether;
-- poly (2-ethyl-6-propyl-1,4-phenylene)ether;

and the like;

most preferred is poly(2,6-dimethyl-1,4-phenylene)ether.

Within the expression "polyphenylene ether (C_1)", as used in the present disclosure and in the appended claims, both homo- and co-polymers containing the structural units of above formula (X) are comprised, such as, e.g., those copolymers which comprise units derived from 2,6-dimethylphenol and 2,3,6-trimethyl phenol; as well as also those graft copolymers which are obtained by grafting onto the polyphenylene ether chain one or more vinylic monomer(s), such as acrylonitrile, or vinyl aromatic compounds, such as styrene; or polymers, such as polystyrene, or elastomers.

The polyphenylene ethers generally have an average molecular weight, as determined by Gel Permeation Chromatography (GPC), comprised within the range of from 5,000 to 120,000, and their intrinsic viscosity is higher than 0.1 dl/g and preferably is comprised within the range of from 0.30 to 0.90 dl/g, as measured in chloroform at 23 °C.

These polyphenylene ethers can be produced by oxidizing a phenolic compound with oxygen or an oxygen containing gas, preferably in the presence of a catalyst for oxidative coupling, as disclosed in U.S. patent Nos. 3,226,361; 3,234,183; 3,306,874; 3,306,875; 3,257,357; 3,257,358; 3,337,501; 3,787,361; 3,956,242; 3,962,181; 3,965,069; 4,075,174; 4,093,595-598; 4,102,865; 4,184,034; 4,385,168, and so forth.

Additionally to components (C_1) and (C_2), the compositions according to the present invention may also contain reinforcer additives, such as, e.g., fiberglass, carbon fibres, high-modulus organic and inorganic fibres, metal fibres, inorganic fillers, and so forth, as well as flame retardant agents, dyes, pigments, stabilizers, lubricants, and so forth, all of which are well known for those skilled in the art.

The reinforcer additives can be used in amounts which generally are not larger than 50% by weight, and preferably not larger than 30% by weight, based on total composition weight.

Suitable stabilizers to be used in the compositions according to the present invention comprise many from well known suitable heat and oxidation stabilizers, as generally used for polyphenylene ether resins or for high-impact vinyl aromatic polymers. For example, liquid phosphates and sterically hindered phenols can be added to the compositions according to the present invention, in amounts which may range from 0.05 to 5% by weight.

The compositions according to the present invention can be prepared by means of any conventional compounding methods. For example, the compounding can be carried out in the molten state and the mixing time and temperature values are selected and determined according to the composition. Temperatures are generally comprised within the range of from 200 to 300 °C.

Any blending units can be used. The method can be either continuous or batchwise. More specifically, single-screw or twin-screw extruders, internal compounders of Banbury type, blending rollers, and the like, can be used.

Whilst all of the components of the composition can be added since the beginning of the compounding step, and directly to the compounding unit, in some cases the polymodal block polymer (i) is preferably pre-blended with the vinyl aromatic polymer containing the dienic rubber in the form of fine particles (ii), before blending step with the polyphenylene ether (C_1).

The compositions according to the present invention are easily processed by injection moulding or extrusion and display a set of properties which make them suitable for use in the production of formed articles having high-impact strength, together with a good heat resistance. Thanks to these properties, the compositions according to the present invention find applications in the sectors of haulage and road transport, for the production of manufactured articles which can be oven painted, parts coming into contact with the engine, household appliances, electronic articles and technical articles in general, as sumps, boxes, containers, panels, sheets, rods, and so forth.

In order to better understand the present invention and to practice it, in the following some illustrative examples are reported which in no way shall be construed as being of limitative character.

In the examples for the determination of the characteristics of the thermoplastic compositions obtained, the following methods were used:

Mechanical properties

The IZOD notched resilience at 23 °C according to ASTM D 256, on specimens of 3.2 and 12.7 mm of thickness, the yielding strength, the tensile strength, the elongation at break and elastic modulus according to ASTM D 638, were determined

Thermal properties

The VICAT softening point under 1 kg and at 5 kg in oil was determined according to the standard ISO 306 procedure.

Rheologic properties

The Melt Flow Index (M.F.I.) was determined according to the standard ASTM D 1238 procedure, at 260 °C and under a load of 5 kg was determined.

Examples 1-3

The following components were blended on a compounder unit of drum tumbler type, at room temperature:

-- poly(2,6-dimethyl-1,4-phenylene) ether (PPE) having an intrinsic viscosity of 0.54 (in chloroform at 23 °C); used in such amounts as reported in Table 1;

-- a polymodal radial block polymer (i) of styrene-butadiene type, having the above reported structure (VII), comprising 20-21% by weight of butadiene and 79-80% by weight of styrene, and containing silicon as the coupling radical. This polymer is marketed by the company BASF under the trade mark STYROLUX(R) 684 D, and was used in such amounts as reported in Table 1; and

-- a high-impact polystyrene (HIPS) (ii) containing 10.5% by weight of polybutadienic rubber in the form of particles having an average chord of 2.5-3.0 micrometres (as determined by transmission microscopy), a product manufactured by the present Applicant. It was used in such amounts as reported in Table 1.

The resulting compound was dried at 80 °C for 4 hours and was extruded by means of a single-screw BANDERA TR 45 extruder, with a length:diameter ratio of 25, with gas venting, at the temperature of 220 °C.

By cutting the noodles exiting the extruder, pellets were obtained which were dried at 80 °C during 4 hours.

For the determination of the characteristics, the pellets were injection moulded at a temperature of 240-260 °C on an injection moulding press NEGRI & BOSSI V-17-110 FA, in order to obtain the specimens having such dimensions as required by the standards.

The properties measured on the resulting specimens are reported in Table 1.

Table 1

Components	Examples		
	1*	2*	3
-- PPE (% by weight)	42	42	42
-- STYROLUX(R) 684D (% by weight)	58	--	43.5
-- HIPS (% by weight)	--	58	14.5
MECHANICAL PROPERTIES			
-- IZOD 3.2 mm (J/m)	70	125	300
-- IZOD 12.7 mm (J/m)	60	105	230
-- Yielding strength (N/mm^2)	42	50	43
-- Tensile strength N/mm^2)	38	51	39
-- Elongation at break (%)	30	75	70
-- Elastic modulus (N/mm^2)	2150	1950	2100
THERMAL PROPERTIES			
-- VICAT Softening point / 1 kg (°C)	134	144	138
-- VICAT Softening point / 5 kg (°C)	118	135	122
RHEOLOGIC PROPERTIES			
-- M.F.I. (g/10 min)	1,5	1	1,2

* Comparison Examples

Example 4

The operating modalities of Example 3 were repeated, with STYROLUX(R) 684 D being replaced by STYROLUX(R) 2686. This product is marketed by the company BASF and is a polymodal radial styrene-butadiene block polymer containing approximately 26% by weight of butadiene and approximately 74% by weight of styrene, and silicon as the coupling agent.

The properties of the resulting compound are:

MECHANICAL PROPERTIES	
-- IZOD 3.2 mm	360 J /m
-- IZOD 12.7 mm	290 J /m
-- Yielding strength	44 N/mm^2
-- Tensile strength	42 N/mm^2
-- Elongation at break	74 %
-- Elastic modulus	2150 N/mm^2

THERMAL PROPERTIES	
-- VICAT Softening Point under 1 kg	137.5 ° C
-- VICAT Softening Point under 5 kg	123 ° C

Examples 5-9

The operating modalities of Example 1 were repeated with STYROLUX(R) 684 D being replaced by FINCLEAR(R) 520, which was used in such amounts as reported in Table 2. FINCLEAR(R) 520 is a polymodal linear styrene-butadiene block polymer having the above reported structure (I), containing a tapered block between B and S_2, and having a content of styrene of 74% by weight, and of 26% of

butadiene, by weight.

The characteristics of the resulting compounds are reported in following Table 2:

Table 2

Components	Examples				
	5*	6	7	8	9
-- PPE (% by weight)	42	42	42	20	20
-- FINACLEAR(R) 520 (% by weight)	58	43.5	29	60	40
-- HIPS (% by weight)		14.5	29	20	40
MECHANICAL PROPERTIES					
-- IZOD 3.2 mm (J/m)	70	350	250	400	350
-- IZOD 12.7 mm (J/m)	58	270	170	300	270
-- Yielding strength (N/mm^2)	45	46	46	29	28
-- Tensile strength N/mm^2)	41	45	46	28	30
-- Elongation at break (%)	50	78	80	115	90
-- Elastic modulus (N/mm^2)	1900	1950	1950	1400	1400
THERMAL PROPERTIES					
-- VICAT 1 kg (°C)	135	138	140	113	115
-- VICAT 5 kg (°C)	119	121	125	90	97

* Comparison Examples

Claims

1. Moulding composition having an extremely good combination of physical-mechanical, tensile and thermal properties, comprising a polyphenylene ether and a high-impact vinyl-aromatic polymer, characterized in that said high-impact vinyl aromatic polymer is constituted by a blend of a polymodal vinyl aromatic monomer- conjugated diene block polymer and a high-impact vinyl-aromatic polymer containing, dispersed in it, a dienic rubber, in the form of particles having a cellular structure and an average chord of at least 1.2 micrometres.

2. Moulding composition according to claim 1, characterized in that it comprises:

(C_1) a polyphenylene ether, and

(C_2) a high-impact vinyl aromatic polymer constituted by a blend of

(i) a polymodal vinyl aromatic monomer-conjugated diene block polymer, having a content of vinyl aromatic monomer comprised within the range of from 55 to 85% by weight, and

(ii) a vinyl-aromatic polymer containing from 5 to 15% by weight, based on said polymer, of a dispersed dienic rubber in the form of particles having a cellular structure and an average chord of at least 1.2 micrometres.

3. Moulding composition according to claim 1 or 2, characterized in that said component (C_1) is present in amounts of at least 1% by weight, and said component (C_2) is present in amounts of at least 20% by weight, based on total composition.

4. Moulding composition according to any of the preceding claims, characterized in that it contains:

* from 5 to 60% by weight of polyphenylene ether (C_1) and, correspondingly
* from 95 to 40% by weight of the high-impact vinyl aromatic polymer (C_2);

with said percent levels being referred to the total weight of the blend.

5. Moulding composition according to any of the preceding claims, characterized in that it contains:

* from 20 to 45% by weight of polyphenylene ether (C_1) and, correspondingly

* from 80 to 55% by weight of high-impact vinyl aromatic polymer (C_2);

with said percent levels being referred to the total weight of the blend.

6. Moulding composition according to any of the preceding claims, in which the high-impact vinyl aromatic polymer (C_2) contains from 30 to 90% by weight of polymodal block polymer (i) and, correspondingly, from 70 to 10% by weight of vinyl aromatic polymer (ii) containing the dienic rubber in the form of dispersed particles.

7. Moulding composition according to claim 6, in which the polymodal block polymer (i) is present at a level comprised within the range of from 50 to 85% by weight and, correspondingly, the high-impact vinyl aromatic polymer (ii) is present at a level comprised within the range of from 50 to 15% by weight.

8. Moulding composition according to any of the preceding claims, in which the polymodal block polymer (i) is of linear type, having the general formula (I) or (II):

(I) S_1-B-S_2;

(II) B_1-S_1-B_2-S_2;

in which: S_1 and S_2 are non-elastomeric polymeric blocks of a vinyl aromatic monomer having different molecular weights; and B, B_1 and B_2 are elastomeric polymeric blocks based on a conjugated diene, having the same, or different molecular weights; said non-elastomeric polymeric blocks having a molecular weight comprised within the range of from 5,000 to 250,000 and said elastomeric blocks having a molecular weight comprised within the range of from 2,000 to 250,000.

9. Moulding composition according to claim 8, in which between the polymeric blocks S_1, S_2 and B, B_1 and B_2, "random" and/or "tapered" chain portions are present.

10. Moulding composition according to any of the preceding claims from 1 to 7, in which the polymodal block polymer (i) is of radial type, having one of following general formulae from (III) to (VIII):

(III) $(S_1\text{-}S_2\text{-}B_1)_n - X - (B_1 - S_2)_m$;

(IV) $(S_1\text{-}S_2/B_1\text{-}B_2)_m - X - (B_2\text{-}B_1/S_2)_n$;

(V) $(S_1\text{-}S_2\text{-}B_1/S_3\text{-}B_2)_m - X - (B_2\text{-}S_3/B_1\text{-}S_2)_n$;

(VI) $(S_1\text{-}B_1 \rightarrow S_2)_n - X - (S_2 \leftarrow B_1)_m$;

(VII) $(S_3\text{-}S_4\text{-}B_2 \rightarrow S_5)_n - X - (S_5 \leftarrow B_2\text{-}S_4)_m$

(VIII)
$$\begin{matrix} (S_6\text{-}S_7\text{-}B_3\text{-}S_8\text{-}B_4)_p \\ \backslash \\ (S_7\text{-}B_3\text{-}S_8\text{-}B_4)_q\text{-}X \\ / \\ (S_8\text{-}B_4)_r \end{matrix}$$

wherein:

S_1, S_2, S_3, S_4, S_5, S_6, S_7, and S_8 are non-elastomeric polymeric blocks, of a vinyl-aromatic monomer, each having different molecular weights, thus yielding bimodal, trimodal, or, in general, polymodal blocks;

B_1, B_2, B_3 and B_4 are elastomeric polymeric blocks based on a conjugated diene, having the same molecular weight or different molecular

	weights from one another;
X	is the radical of a polyfunctional coupling agent, by means of which the block copolymers forming the arms are chemically coupled with one another;
m and n	are integers, with m being larger than n, and the sum of which is larger than 3, generally comprised within the range of from 3 to 10 and preferably is either 3 or 4, and corresponds to the functionality of radical X; and
p, q and r	are integers the sum of which is larger than 3, generally comprised within the range of from 3 to 10 and preferably is either 3 or 4, and corresponds to the functionality of radical X; and
S_2/B_1, B_1/S_2, B_1/S_3 and S_3/B_1	are blocks of copolymers of either "random" and/or "tapered" type of vinyl aromatic monomer and conjugated diene.

11. Moulding composition according to claim 10, in which the non-elastomeric polymeric blocks have a molecular weight comprised within the range of from 5,000 to 250,000, the elastomeric polymeric blocks have a molecular weight comprised within the range of from 5,000 to 50,000, the copolymer blocks of "random" and/or "tapered" type have a molecular weight comprised within the range of from 500 to 50,000, and the blocks $B_1 \rightarrow S_2$ and $B_2 \rightarrow S_5$ preferably have a molecular weight comprised within the range of from 10,000 to 100,000.

12. Moulding composition according to any of the preceding claims, in which the high-impact vinyl aromatic polymer (II) is produced by polymerizing a vinyl aromatic monomer and a dienic rubber.

13. Moulding composition according to claim 12, in which the content of dienic rubber in the high-impact vinyl aromatic polymer (II) is comprised within the range of from 5 to 15%, preferably of from 7 to 12% by weight.

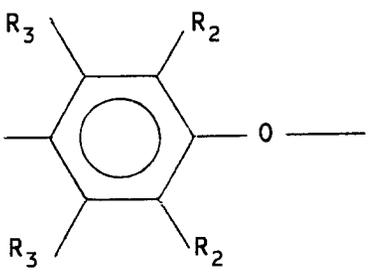
14. Moulding composition according to claim 12 or 13, in which the average chord of dienic rubber particles is comprised within the range of from 1.2 to 15, preferably of from 1.5 to 10 micrometres.

15. Moulding composition according to any of the preceding claims, in which the vinyl aromatic monomer is styrene.

16. Moulding composition according to any of the preceding claims, in which the conjugated diene is 1,3-butadiene.

17. Moulding composition according to any of the preceding claims, in which the dienic rubber is selected from a polymer of a conjugated diene having from 4 to 6 carbon atoms, such as polybutadiene, high-cis and medium-cis polybutadiene and low viscosity polybutadiene, polyisoprene, and a butadiene and/or isoprene copolymer with styrene or other monomers containing more than 50% by weight of butadiene or isoprene.

18. Moulding composition according to any of the preceding claims, in which the polyphenylene ether (C_1) comprises a plurality of structural units of formula (X):



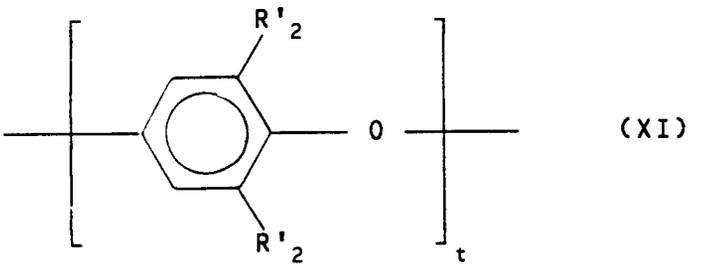
(X)

wherein:

each R_2 independently is a halogen atom, a primary or secondary C_1-C_7 alkyl, substituted alkyl, phenyl, substituted phenyl, C_1-C_7 alkyloxy or halo-alkyloxy radical in which at least two carbon atoms separate the halogen and oxygen atoms; and

each R_3 independently is a hydrogen atom, a halogen atom, a primary or secondary C_1-C_7 alkyl, substituted alkyl, phenyl, substituted phenyl, C_1-C_7 alkyloxy or halo-alkyloxy radical, as defined for R_2.

19. Moulding composition according to any of the preceding claims, in which the polyphenylene ether (C_1) has the general formula (XI):



(XI)

wherein the radicals

R'_2 independently are an alkyl radical having from 1 to 4 carbon atoms and

t is at least 50 and preferably is comprised within the range of from 60 to about 600.

20. Moulding composition according to any of the preceding claims, in which said polyphenylene ether (C_1) is poly(2,6-dimethyl-1,4-phenylene)ether having an average molecular weight, as determined by Gel Permeation Chromatography (GPC), comprised within the range of from 5,000 to 120,000, and having an intrinsic viscosity higher than 0.1 dl/g, and preferably comprised within the range of from 0.30 to 0.90 dl/g, as measured in chloroform at 23 °C.

21. Moulding composition according to any of the preceding claims, additionally containing reinforcer additives, such as fiberglass, carbon fibres, high-modulus organic and inorganic fibres, metal fibres, inorganic fillers, and so forth, as well as flame retardants, dyes, pigments, stabilizers, lubricants, and so forth, in an amount not higher than 50% by weight and preferably not higher than 30% by weight, based on total composition weight.